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(19) (CA) **APPLICATION FOR CANADIAN PATENT** (12)

(54) Low Molecular Weight Polysaccharide Derivatives Useful  
Food Ingredients

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Abstract of the Disclosure

A mixture of polymers derived from degradation of a polysaccharide derivative is used as new low calorie food ingredient and also to replace at least a portion of a conventional high calorie ingredient in a foodstuff recipe, the fat substitute being fat-free and having fat-like properties such that the eating quality of the new food products or the high calorie ingredient-replaced foodstuff is desirable or substantially maintained.

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accompanying drawings and entitled:  
LOW MOLECULAR WEIGHT POLYSACCHARIDE DERIVATIVES  
USEFUL FOOD INGREDIENTS

#### RELATED APPLICATIONS

This is a continuation-in-part of U.S. Patent Application Serial No. 464,219 filed January 12, 1990, which is a continuation-in-part of U.S. Patent Application Serial No. 370,629 filed June 23, 1989, which is a continuation-in-part of U.S. Patent Application Serial No. 309,387 filed February 10, 1989, the contents of all of the above-identified applications are hereby expressly incorporated by reference.

The contents of Applicants' co-pending related applications entitled "Paper Composition and Uses Therefor" and "Polysaccharide Article and Uses Therefor", filed concurrently herewith are also expressly incorporated by reference.

#### FIELD OF THE INVENTION

This invention relates to the production and use of a new food ingredient which is fat-free having fat-like properties. In particular the fat-like properties of the new ingredient imparts an acceptable eating quality to conventional food recipes, such that it can be used as a component in making food or can be used to replace, in part or

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full, the ordinary fat or carbohydrate content in various food products. The invention also further relates to methods for producing food products, which contain such a new ingredient and which may be used as a fat or carbohydrate substitute.

#### BACKGROUND OF THE INVENTION

Numerous studies throughout the world have shown a link between a fatty diet high in cholesterol, and heart diseases. Also, because of its high energy content (about 9 kcalories/g) high fat consumption may cause obesity and its associated problems. It is recommended (by e.g. The American Heart Association) that fat consumption should be reduced so that no more than 30% of caloric energy is derived from fat. It has also been recommended that an increased proportion of calorie intake should be obtained from complex carbohydrates rather than fat. Fat in the diet should thus be partially omitted or substituted. However, fat endows desirable eating qualities (e.g. taste, mouthfeel, aroma, consistency) and consumers are used to and enjoy the properties that fat lends to food. So substitution of fat with a non-fat substance that is fat-free but has fatty consistency and mouthfeel would be an attractive approach to this problem.

Cellulose derivatives such as

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carboxymethylcellulose, methylcellulose, hydroxypropylmethylcellulose and hydroxypropylcellulose are non-caloric (non-metabolizable by humans or intestinal flora in human beings), odorless, tasteless water-soluble polymers derived from cellulose. They dissolve rapidly in cold and hot water and are physiologically inert.

The production of different types of starch derivatives has been described, e.g. in Radley, J.A. Starch And Its Derivatives, 4 ed. [p. 382] 1968 and in Rutenberg et al., Starch: Chemistry and Technology, 2ed., pp. 311-88 (1984). Derivatives such as oxidized starches, cross-linked starches, starch ethers and cationic starches are discussed in the foregoing. One or more of the inventors herein have also shown the production and use of higher molecular weight polysaccharides, including starch and cellulose derivatives, in a variety of different applications in U.S. Patent Nos. 4,810,646; 4,851,393; 4,749,620; 4,744,933; 4,739,693; 4,732,205; 4,119,783; 4,666,492 and have also demonstrated the production and use of degraded cellulose derivatives as food ingredients in co-pending U.S. Patent Application Nos. 309,387; 370,629 and 464,291 from which this application derives priority as to common subject matter

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expressly and inherently disclosed therein.

Carboxymethyl starch (CM starch) is an ether type starch derivative typically prepared by the reaction of chloroacetic acid on starch in the presence of alkali. The sodium salt of CM starch, which occurs also under the name sodium starch glycolate, is used as a disintegrant in pharmaceutical tablets. Other proposed or actual usages are, e.g. components of absorbents, adhesives, medical poultices, thickening agents, stabilizers, papermaking, coating and pulp refining. CM amylose has been suggested to be used to lower the blood sugar level or as blood volume expander. It has been used as a substrate when studying the kinetics of amylases. CM starch is insoluble in cold water, but it has high water absorption properties such that CM starch particles swell to several times their original volume.

Maltodextrin, enzymatically hydrolysed starches, are commercially available. However, these products are less suitable as fat substitutes in many types of fat containing foods, especially when a high proportion of fat is replaced.

There are also some new developments in the area of low-calorie fat mimetics that have been recently approved or are awaiting regulatory approval. They have been made, e.g. by modifying natural proteins

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physically or by modifying sucrose chemically. However, many of these compounds suffer from severe dietary and functional shortcomings.

#### SUMMARY OF THE INVENTION

Therefore, it is an object of the present invention to provide a new functional food ingredient which can be produced by partial degradation of conventional polysaccharide derivatives which is useful by itself as a new food ingredient and as a fat or carbohydrate substitute having fat-like properties for use in food products.

The invention discloses the use and manufacture of novel water soluble or water suspendable mixtures of relatively low molecular weight polymers obtained by degrading or hydrolysing or fractionating polysaccharide derivatives, and most preferably degraded starch and cellulose derivatives.

In accordance with the invention there is provided a water soluble or water suspendable mixture of polymers derived from a polysaccharide derivative. The mixture of polymers can be used in a foodstuff composition. The mixture has an average degree of polymerization in the range of 5 to 500 as determined, in the case of starch derivatives, by the reducing end group measurement as described for example in Somogyi, M., J. Biol. Chem., Vol. 195,

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pp. 19-33 (1952), the disclosure of which is incorporated herein by reference. The most preferred polysaccharide derivative comprises a starch or cellulose derivative.

The polysaccharide derivative may be degraded by enzymatic, chemical or physical or mechanical means. In embodiments where an enzyme preparation is utilized to perform the degradation, the enzyme preparation is typically selected from the group of polysaccharide degrading enzymes specific to the particular polysaccharide. In the case of starch derivatives, enzymes such as amylases or pullanases and mixtures thereof are suitable.

In embodiments where degradation of a polysaccharide derivative is to be effected by chemical or physical means, chemical hydrolysis, chemical oxidation, heat or sonic treatment are preferred mechanisms for achieving the desired polymeric mixtures according to the invention.

By conventional means a polysaccharide derivative or an initially degraded polysaccharide derivative mixture may be further separated into fractions of polymers of differing average chain lengths. The viscosity of the various fractions will vary with the degree of average chain length of the polymers contained within in a fraction. Depending on the particular foodstuff application,



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the invention further contemplates selecting one or more fractions from an initial polymeric mixture having a viscosity (average chain length) which is most appropriate for the particular foodstuff application. The selection of a particular average chain length fraction and the amount of such a fraction to be used in any given foodstuff application may vary according to the amount of fat or carbohydrate to be replaced, it being recognized that the higher the absolute amount of substitution agent desired to be used in a particular foodstuff, the lower the viscosity (average molecular weight) of the fraction of mixture of polymers which should be used.

The invention further contemplates removing all or a portion of the fat content contained in the composition of a foodstuff and substituting therefor a mixture of polymers produced according to the invention for the removed fat such as saturated triglyceride of fatty acid, phospholipids and cholesterol containing materials such as butter, oil, and mayonnaise. The mixture of polymers produced according to the invention could also be used to replace all or a portion of the carbohydrate content contained in a foodstuff. Typical carbohydrates which might be replaced are starch, dextrin, sucrose, glucose, maltose or fructose

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containing foodstuffs such as corn or wheat flour, corn meal, syrup, molasses and the like. Oils and lipids which are normally found in foods such as unsaturated triglycerides, phospholipids and lecithin may also be replaced by the new ingredient of the invention.

The invention therefore provides for a method of preparing a low calorie food product comprising replacing at least part of the high calorie components of a foodstuff with a mixture of polymers having an average degree of polymerization in the range of 5 to 500 derived from degradation of a polysaccharide derivative. Preferably, the new low calorie food ingredient can substitute for at least about 10% of the normal fat or carbohydrate content of a conventional food recipe.

The invention also provides for cake and icing compositions comprising a sweetener, water, fat, and other ingredients, which fat ingredient has some portion thereof substituted with a mixture of polymers derived from a degraded polysaccharide derivative, the mixture having an average degree of polymerization of about 5 to 500.

The invention also provides for cake and icing compositions comprising a sweetener, fat and other ingredients in which the low calorie food ingredient is used as a component of the composition.

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DETAILED DESCRIPTION OF THE INVENTION

This invention describes a new functional food ingredient which can be produced by partial degradation of polysaccharide derivatives. The term "functional" refers to a food ingredient which imparts some property to the food or produces some effect. The term "polysaccharide" refers to a polymeric carbohydrate having a plurality of repeating units comprised of simple sugars. The degradation product is comprised of a mixture of relatively low molecular weight polymers. The term "polymeric" or "polymer" is meant to include both polymeric units and oligmeric units of the polysaccharide derivatives of the invention. Polymeric units or polymers comprise between about 4 and about 10 repeating units.

CM starch can be hydrolyzed enzymatically to produce CM starch hydrolysates. According to this invention, the suspensions or gels prepared from these hydrolysates have fat-like properties and are similar to fat in mouthfeel and in handling properties. CM starch is easily hydrolyzed with commercial amylases, and even mild hydrolysis may produce preparations suitable for use as fat replacers. CM starch can be made from various sources of starch including wheat, rice, tapioca corn and potato starch. Potato starch, a typical

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starting material, contains about 20% amylose (DP of about 3,000) and about 80% amylopectin (DP of about 2,000,000). This molecular composition is particularly suitable as a fat replacer. Other typical suitable starch may be corn starch, wheat starch and other major grain starch. The derivatives of this invention include hydroxypropyl, methylethyl and hydroxyethyl starches.

The term "derivative" is meant to define polysaccharides according to this invention that are substituted. Preferably the polysaccharide derivative starting material has a degree of substitution of between about 0.1 to about 3.0. "Degree of substitution" refers to the number of derivative groups (e.g. carboxymethyl, hydroxypropyl) per monomer units in the polysaccharide backbone (branched or straight chain). A degree of substitution of 0.2 would mean, for example, that there is about one derivative substituent per every 5 monomer units in the polysaccharide polymer. A degree of substitution of three (3) would mean there are three derivative substituents per every monomer unit in a polysaccharide chain.

The derivative substituents are typically bonded to a starch glucose monomer unit at the 2, 3 and 6 positions. Most typically a starch starting

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material comprises between about 1% to 85% amylose and about 15% to 99% amylopectin.

Cellulose derivatives are commercially available. Such exemplary products as methylcellulose (MC, Methocel MC, 64630, Fluka Chemie AG, CH-9470 Buchs, Switzerland), hydroxypropylmethylcellulose (HPMC, H-9262, Sigma Chem. Co., St. Louis, MO) and carboxymethyl cellulose (CMC 7MFD, Blanose, Hercules Chem. Co., 92507 Rueil-Malmaison Ceder, France) all have a degree of substitution between 0.1 and 3. Hydroxypropyl celluloses are also commercially available and suitable for use in producing a degraded polysaccharide derivative according to the invention.

Other polysaccharide derivatives having a polymer backbone including one or more sugar monomers such as glucose, galactose, arabinose, mannose, fructose, rhamnose, and xylose are suitable starting materials. Such polymer backbones may be branched or straight. Examples of such polysaccharides are starch, cellulose, pullulan, pustulan, laminarin, scleroglucan, carragenan, alginate, guar gum, gum arabic, inulin, pectin, whelan, rhamnan, gellan, xanthan, zooglan, methylan, chitin, cyclodextrin and chitosan. Typical derivative substituents which are substituted onto

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such polysaccharides are one or more of sulfate, carboxylic acid (carragenan, alginate, pectin), carboxylic acid ester, pyruvic acid, pyruvate (pectin, xanthan gum, zooglan, methylan), carboxymethyl, hydroxypropyl, methyl, methylethyl, hydroxyethyl, hydroxyethylmethyl and the like.

As described more fully herein, such polysaccharide derivatives may be degraded to polymeric mixtures of average DP between 5 and 500 by enzymatic, chemical physical, or mechanical agents/means. The polymeric mixtures are generally referred to as a "hydrolyzate". The term "degraded" refers to the procedure whereby polysaccharide derivatives are broken down into smaller polymeric units. Exemplary enzymes for use in degrading certain of the above described polysaccharide derivatives are pectinases, lyases, xanthanases, chitinases, lysozymes and laminarases.

Exemplary enzymes which are suitable for degrading cellulose derivatives are various food grade cellulases. They can be produced from a multitude of different microorganisms such as strains of Trichoderma, Aspergillus, Penicillium, etc. A selected microorganism strain is grown by conventional means in a medium containing food grade materials such that the cellulases are produced, the microorganism is separated from the medium, the

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medium is collected and typically concentrated and dried. These enzymes can be used as such or in mixtures and they can be modified in many different ways known to the man skilled in the art. A most preferred enzyme preparation is produced from Trichoderma reesei, from which preparations the beta-glucosidase and/or the cellobiohydrolase activities are removed chromatographically or genetically. Beta-glucosidase and/or cellobiohydrolase activities are preferably removed from the selected cellulase preparation so as to prevent the degradation of the cellulose derivative into mono- and disaccharides. Genetic alteration of the appropriate enzyme producing microorganism may be effected with radiation or mutagenic chemical agents (or by gene inactivation by recombinant DNA methods) so as to disenable production of beta-glucosidase and cellobiohydrolase by the microorganism. Cellulase preparations suitable for use herein are, e.g. the commercially available cellulase preparations designated as the Econase® series as produced by Alko Ltd., Helsinki, Finland.

This invention relates more specifically to a water soluble or suspendable mixture of polymers derived from a polysaccharide derivative using, for instance, such enzymes. The polymeric mixtures are characterized by having an average degree of

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polymerization (DP) in the range of 5-500. A range of about 7 to about 200 is preferred.

Following is a description of some exemplary embodiments of the invention where a degradation treatment is carried out using enzymatic, chemical, physical or mechanical agents/methods.

In one embodiment of the invention a polysaccharide derivative may be hydrolyzed by treating the starch derivative with a solution of acid. Typical acid treatment solutions might contain acids such as sulphuric acid, hydrochloric acid, phosphoric acid, or mixtures of the foregoing. The concentration of the acid in the treatment solution and the treatment time and temperature may vary depending on the degree of degradation of the polysaccharide derivative which is desired. In any event where an acid hydrolysis treatment is utilized, the acid concentration and the treatment time and temperature is selected to produce a mixture of polymers having an average DP of between 5-500, and which most preferably contains less than about 25% by weight of mono- and disaccharides.

In another embodiment of the invention a selected polysaccharide derivative may be degraded by oxidation with such agents as chlorine, oxygen or



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hydrogen peroxide. Such oxidative treatments and reaction conditions are well known in the art. It may also be possible to use physical methods like heat or mechanical shear treatment, or sonication when cleaving the chain backbone of polysaccharide derivatives.

Whatever conventional chemical (hydrolytic, oxidative or otherwise) or physical treatments are employed, the conditions and the degree of treatment are selected such that the polymeric mixture resulting from the initial treatment has an average DP of between 5 and 500, and contains less than about 25% by weight of mono- and disaccharides.

#### Enzyme Treatment For Starch Derivatives

Enzymes which may be used in some embodiments of this invention, e.g. with respect to starch derivatives, are various food-grade amylolytic enzyme preparations. They can be produced from a multitude of different microorganisms such as strains of Bacillus, Klebsiella, Clostridium, Aspergillus, Rhizopus. Typical commercially available enzyme preparations suitable for use herein are amylolytic preparations (such as alpha and beta amylases), pullulanases, and cyclodextrin glycosyltransferases (CGTase).

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Starting Materials

A most preferred polysaccharide derivative for use herein is carboxymethyl starch. The invention is not limited to the use of this polysaccharide derivative, but others, such as hydroxypropyl, methylethyl, hydroxyethyl and other typically lipophilic functional group substituted starches may be more suitable for a specific application.

General Preparation of a Typical Starch Derivative Hydrolysate

In one embodiment of the invention, starch derivative hydrolysates may be prepared from starch derivatives as defined above by an enzymatic hydrolysis utilizing an amyolytic preparation having  $\alpha$ -amylase as the main active hydrolytic agent such that the only insignificant amounts of mono- and disaccharides are produced. The hydrolysis procedure is generally carried out by dissolving the starch derivative in water, adjusting the pH and the temperature to the value suitable for the enzyme activity, adding the enzyme to the solution and allowing the enzyme to react for a suitable time. After the reaction, the enzyme is inactivated by heating the solution up to about 100°C and the hydrolysate product is concentrated and dried. The average degree of polymerization

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(DP) of the polymers formed by such a hydrolysis may be less than 500. The specific conditions suitable for and the specific time sufficient to secure the desirable hydrolysis may be readily determined for each selected starch derivative and each selected enzyme preparation.

Similarly in other embodiments of the invention where degradation is carried out using chemical or physical means, the average DP of the polymers is less than 500. Most preferably in such embodiments, the treatment conditions are selected such that the resulting polymeric mixtures contain less than about 25% by weight of mono- and disaccharides.

#### Use of Oligomeric Mixtures Derived from Starch Derivatives

The degraded starch derivative products of the invention dissolve or suspend rapidly in water and are physiologically inert.

The calorie content of carbohydrates in general is 4 kcal/g, which as such is less than the caloric content of fats (9 kcal/g). Carboxymethyl starch is an ether type starch, and it has been suggested that ether linkages with respect to the derivative in starch are not hydrolysable (Food Technology Review, No. 52, 1979, p. 113). Thus the calorie content of CM starch and its hydrolysates may be even less than 4 kcal/g. According to U.S. Patent 3,505,110,

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another ether type starch, namely hydroxypropylated starch was hydrolysed to a syrup that was found to be amylase resistant. Thus the caloric value of the product was very low, and it was suggested to be used as a substitute for ordinary sugars.

Similarly, the calorie content of various polysaccharides with various functional groups such as carboxymethyl starch are believed to be very low and certainly less than the original polysaccharide or its degraded forms.

The polymeric mixtures and fractions thereof produced according to this invention can be used, for example, as new low calorie fat sparing agents. These mixtures can be used to replace the normal fat or carbohydrate content in various foodstuffs. These mixtures can be used to replace fat in various foodstuffs, like baked goods, butter, butter icing and spreads. All of and at least a substantial portion of fat or carbohydrate can be replaced by these mixtures. The precise amount which can be replaced depends on the application. The texture of the foodstuff and the eating quality of the new product can thus be improved or remain unchanged.

For example, a foodstuff composition can be prepared comprising fat in combination with one or more of the following ingredients, sweeteners (such as sugar or saccharin), art-recognized flours (such

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as wheat and corn flour), emulsifiers (i.e., agents capable of emulsifying the food composition), raising agents (e.g., yeasts), thickeners, and acidifiers. At least some portion of the fat ingredient, preferably at least about 10%, can be replaced with a mixture of polymers derived from the polysaccharide derivatives, described herein. Furthermore, the entire fat component of the foodstuff can be replaced with a mixture of these polymers.

For example, a cake composition can be prepared comprising a sweetener, flour, a raising agent, egg ingredient, water and a fat ingredient. At least a portion of or, optionally, the entire fat ingredient can be substituted by a mixture of polymers derived from a degraded polysaccharide derivative, described herein, in which the mixture has an average degree of polymerization of about 5 to 500. Preferably, at least about 10% of the fat ingredient is replaced.

An icing composition can be similarly prepared by combining a sweetener, water and a fat ingredient. At least a portion of the fat ingredient, or the entire fat ingredient, can be replaced with the mixture of polymers described herein.

By conventional means an initially degraded polysaccharide derivative mixture may be further separated into fractions of polymers of differing

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average chain lengths, i.e. differing average DP. The viscosity of the various fractions will vary with the degree of average chain length of the polymers contained within a fraction. Depending on the particular foodstuff application, one or more fractions from an initially degraded polymeric mixture can be selected having a viscosity (average chain length) which is most appropriate for the particular foodstuff application. The viscosity average molecular weights can easily be determined by a variety of methods. Fractions of hydrolyzate solutions of different viscosity (i.e. molecular weight) can be separated from the original mixture by standard art-recognized separation techniques, e.g. chromatography.

The following examples 1-4 set forth typical exemplary routines for preparing a starch and various starch derivatives hydrolysates therefrom.

Example 1: Starch Derivative Enzymatic Hydrolysis

60 g of carboxymethyl starch (CM starch) derived from potato starch (Primojel; Avebe, 9607 PT Foxhol, The Netherlands) was mixed in 1200 ml of water. The temperature of the mixture was raised to 80°C and the suspension was mixed continuously. 1.5 ml of amylase (Ban 120L, Novo, Industri A/S, Novo Alle, 2880 Bagsvaerd, Denmark) dilution 1/50 by volume was added to the suspension mixture. After hydrolysis of about 30 minutes the enzyme was inactivated by

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heating (100°C, 10 min.). The hydrolysate was then freeze-dried.

The hydrolysate contained negligible amounts of glucose, maltose and oligosaccharides, as the value of reducing sugars was 0.28%. The viscosity of a 5% by weight suspension of the hydrolysate (measured using Haake-Rotovisco RV 12 viscometer with sensor systems NV; Karlsruhe, Federal Republic of Germany) at 25°C was 57 mPa.s (using the shear rate of 692 1/s). The viscosity of the unhydrolysed raw CM starch material was 106 mPa.s (25°C, 692 1/s). Since the viscosity of the hydrolysates is much lower, the hydrolysates can be used at much higher concentration than the original high molecular weight starch derivatives.

#### Use of Degraded Polysaccharide Derivative

The degraded polysaccharide derivatives according to the invention are a new food ingredient in and of themselves and are not necessarily limited to use in conventional food recipes as fat or carbohydrate substitutes although in practical applications such a new low calorie food ingredient is preferably used as a substitute for all or a portion, most preferably at least about 10% of the normal fat or carbohydrate content of a conventional food recipe.

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Example 2 -- Preparation of butter icing using CM starch hydrolysate

A butter icing was prepared with the carboxymethyl starch (CM starch) hydrolysate of Example 1 to replace 33% of the normal fat content of a conventional butter icing recipe. The butter icing contained the following ingredients:

Butter (Fat)	120 g	24%
CM starch hydrolysate (15% by weight suspension in water)	59 g	12%
Icing sugar	225 g	45%
Water	96 g	19%

The CM starch hydrolysate was added to the soft butter, while whisking with electric hand whisk. After that the icing sugar was added. Finally water was added slowly and whisking was continued until the emulsion was light and even.

The resultant butter icing had a good, even texture and a pleasant mouthfeel.

In the recipe above, the butter (fat) content would normally be about 180 g.

Example 3 -- Preparation of butter icing using CM starch

A butter icing was prepared with non-degraded high molecular weight carboxymethyl starch (CM



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starch) to replace 33% of the normal fat content.  
The butter icing contained the following ingredients:

Butter	120 g	24%
CM starch (5% by weight suspension in water)	59 g	12%
Icing sugar	225 g	45%
Water	96 g	19%

The high molecular weight CM starch suspension was added to the soft butter, while whisking with electric hand whisk. After that the icing sugar was added. Finally water was added slowly while still whisking.

No emulsion was formed, but water and oil were immediately separated resulting in an unsuitable food product. When a 10% suspension of non-degraded CM starch was used instead of 5% suspension, the same result was obtained.

Example 4 -- Preparation of butter icing using maltodextrin

A commercial maltodextrin was used to replace 33% of the normal fat content in butter icing. This maltodextrin is manufactured by enzymatic hydrolysis

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of potato starch and has been recommended to be used as a fat replacer, e.g. in mayonnaises, salad dressings, spreads and fillings. The butter icing contained the following ingredients:

Butter	120 g	24%
Maltodextrin (25% by weight suspension in water)	59 g	12%
Icing sugar	225 g	45%
Water	96 g	19%

The maltodextrin suspension was added to the soft butter, while whisking with electric hand whisk. The icing sugar was subsequently added. Finally the water was added slowly while still whisking.

The resultant icing curdled and was very unstable.

Example 5 -- Preparation of Madeira cake using CM starch hydrolyzate

The CM starch hydrolysate of Example 1 was used to replace 40% of the normal fat content in a Madeira cake recipe containing the following ingredients:

Cake Flour	100 g	21 %
Sugar - caster	125 g	26 %

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Butter	39 g	8 %
CM starch hydrolysate (15% by weight suspension)	26 g	5 %
Skimmed milk powder	8 g	2 %
Baking Powder	6 g	1 %
Salt	1.5 g	0.3 %
Water	90 g	19 %
Egg	88 g	18 %

The normal butter content in the above recipe is 65 g. The dry ingredients were mixed in a bowl. The water, fat and the CM starch hydrolysate were added. Using an electric hand whisk, the mixture was mixed on speed 1 (lowest speed) for 30 seconds and on speed 3 (highest speed) for 30 seconds. The egg was then added over 30 seconds on speed 1 and mixing was continued on speed 2 for 135 seconds. Batter was poured into greased tins and baked at 170°C for about 35 minutes.

The modified cake was evaluated and compared with a full fat Madeira cake. The standard cake had slightly more coarse crumb than the modified cake, with 40% fat replaced by CM starch hydrolysate. Both cakes were found to have a pleasant appearance, taste and mouthfeel.

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Example 6 -- Partial replacement of normal fat content in butter

The CM starch hydrolysate the production of which is described in Example 1 was used to replace 33% of the normal fat content in a conventional butter by mixing 10 g of conventional butter with 5 g of CM starch hydrolysate (15% by weight suspension in water). A good shiny and stable emulsion was formed similar to butter.

Example 7: Preparation of a Cellulose Derivative Hydrolysate

In one embodiment of the invention, cellulose derivative hydrolysates may be prepared from soluble cellulose derivatives as discussed above by an enzymatic hydrolysis utilizing a cellulase preparation having endo- 1, 4- beta-glucanase as the sole active hydrolytic agent such that only insignificant amounts of mono- and disaccharides which are absorbed in human intestine (e.g., glucose) or hydrolyzed by the intestinal bacterial flora (e.g., cellobiose), are produced. On the other hand the average degree of polymerization (DP) of the polymers formed by such a hydrolysis is less than 500, and thus the viscosity of solutions of the hydrolysate is reduced significantly compared to the viscosity of solutions of the unhydrolysed cellulose derivatives. The specific conditions suitable for

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and the specific time sufficient to secure the desired hydrolysis may be readily determined for each selected cellulose derivative and each selected enzyme preparation.

Similarly in other embodiments of the invention where degradation is carried out using chemical or physical means, the average DP of the polymers is less than 500 and the viscosity of the resulting mixture is significantly reduced. Most preferably in such embodiments, the treatment conditions are selected such that the resulting polymeric mixtures most preferably contain less than about 5% (and at least less than about 25%) by weight of mono- and disaccharides.

#### A Cellulase Preparation

The beta-glucosidase activity was removed by ion exchange chromatography from the commercially available cellulase preparation, Econase CE, as so designated by Alko Ltd., Helsinki, Finland which was produced from a strain of Trichoderma reesei. The cellulase preparation (column A, Table I) was passed through a cation exchange column (S-Sepharose FF, Pharmacia, LKB Biotechnology AB, Uppsala, Sweden) which was equilibrated with 50 mM sodium acetate pH 3.8 equilibrium buffer. The unbound protein (including polymer producing endoglucanases) was

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washed out with the equilibration buffer (column B, Table 1). Beta-glucosidase activity remained bound to the column and could be separately eluted with 1M NaCl.

TABLE 1

Enzyme	Relative Enzyme Activity (%)	
	<u>A</u>	<u>B</u>
	before ion exchange procedure	after ion exchange procedure
Beta-glucosidase	100	0
endo-1, 4, -beta-glucanase	100	70

Endo- 1, 4- beta-glucanase and beta-glucosidase activities were measured as described by Bailey & Nevalainen (1981): Enzyme Microb. Technol. 3: 153-157. The relative enzyme activities reported in Table 1 of the Econase preparations before and after passage through an ion exchange column demonstrate the results of a typical means according to the invention of preparing an essentially beta-glucosidase free preparation for use in producing the polymeric hydrolysates contemplated by the invention.

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Although Table 1 reports relative enzyme activities, the absolute amount of enzyme used in any particular example is hereafter reported in terms of the amount of enzyme activity of the enzyme employed according to the universal activity unit of nano-katal (nkat) which stands for that amount of enzyme which produces one nanomole of reaction product in one second. (In the context of this application a hydrolysate reaction product such as an polymer which is capable of reducing an agent such as dinitrosalicylic acid which is reduced by the hydrolysate reaction product and subsequently measured.) The method of Bailey et. al., Enzyme Microb. Technol., Vol. 9, pp. 153-157 describes how such measurements of enzyme activity can be made using glucose as a standard.

#### Cellulose Derivative Hydrolyses

##### a. Methylcellulose hydrolysate

30 g of methylcellulose (MC, Methocel MC, 64630, Fluka Chemie AG, CH-9470 Buchs, Switzerland) was mixed in 3 l of water and the pH of the solution was adjusted to 5.5 with 15% phosphoric acid and the temperature was raised to 40°C. 0.3 ml of the enzyme preparation having a total endo-1, 4 beta-glucanase activity of 1680 nkat from which the beta-glucosidase activity was removed chromatographically (as described above) was added

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to the solution. After hydrolysis for 24 hours the enzyme was inactivated by heating ( $90^{\circ}\text{C}$ , 15 min.). The hydrolysate solution was subsequently cooled and freeze-dried.

The hydrolysate product contained less than 0.5% by weight of glucose and cellobiose.

b. Hydroxypropylmethylcellulose hydrolysate

20 g of hydroxypropylmethylcellulose (HPMC, H-9262, Sigma Chemical Company, St. Louis, MO, U.S.A.) was mixed in 1 l of water and the pH of the solution was adjusted to 5.5 with 15% phosphoric acid and the temperature was raised to  $40^{\circ}\text{C}$ . 0.24 ml of the enzyme preparation having a total endo-1, 4 beta-glucanase activity of 1340 nkat from which the beta-glucosidase activity was removed chromatographically (as described above) was added to the solution. After two hours another 20g of hydroxypropylmethylcellulose was added to the solution. After the hydrolysis of 22 hours the enzyme was inactivated by heating ( $90^{\circ}\text{C}$ , 15 min.). Finally the hydrolysate solution was cooled and freeze-dried.

The product contained less than 0.05% by weight of glucose and cellobiose.



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c. Carboxymethylcellulose hydrolysate

Carboxymethylcellulose (CMC) hydrolysates can be prepared by enzymatic, chemical or physical methods as disclosed in co-pending U.S. Patent Applications Serial Nos. 07/309,387, 07/370,629 and 07/464,291. CMC hydrolysates used in the present invention have the average degree of polymerization in the range of 5 to 500, based on the viscosity average molecular weight. The viscosity average molecular weights of the CMC hydrolysates were calculated using the Mark-Houwink equation:

$$[\eta] = KM_v^a$$

where  $[\eta]$  is intrinsic viscosity,  $M_v$  is the viscosity average molecular weight of the polymer and  $K$  and  $a$  are hydrodynamic constants characteristic of the particular polymer-solvent system. The values of  $K$  and  $a$  for CMC, which were used in this study, were  $K = 0.043$  in 0.2 M NaCl and  $a = 0.76$  in 0.2 M NaCl as described in Brown and Henley, Studies on Cellulose Derivatives Part IV. The Configuration of the Polyelectrolyte in Sodium Chloride Solutions, Macromol. Chem., Vol. 79, 68-88 (1964). It is noted that a variety of methods for determining average molecular weights exist, and therefore the values of average molecular weights determined, as well as the average DP values calculated from them, depend upon the experimental

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method and the basis of calculation. CMC hydrolysates have an intrinsic viscosity typically between 50 ml/g - 3 ml/g when measured in 0.2 M NaCl solution. The CMC hydrolysates have the viscosity value in the range of from 5 to 100 mPa.s, when measured in 20% (by weight) solution at 25°C with shear rate  $584s^{-1}$  using a Haake Viscotester, VI 500 with sensor system NV (Karlsruhe, Federal Republic of Germany).

(1) Hydrolysis with Trichoderma reesei derived enzyme preparation

20 kg of carboxymethylcellulose (CMC 7MFD-type, a cellulose gum, also designated by the tradename Blanose and available from Hercules Chemical Company, 92507, Rueil-Malmaison Ceder, France; 7MFD designating a medium viscosity, food grade carboxymethylcellulose having 7 out of 10 glucose units substituted with carboxymethyl) was mixed in 320 l of water and the pH of the solution was adjusted to 5.5 with 15% phosphoric acid and the temperature was raised to 40°C. 0.27 l of the enzyme preparation having a total endo-1, 4 beta-glucanase activity of 1,780,000 nkat from which the beta-glucosidase activity was removed chromatographically (as described above) was added

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to the CMC solution. After one hour another 23 kg of CMC was added to the solution. After hydrolysis of 23 hours the enzyme was inactivated by heating (90°C, 15 min.). Finally, the hydrolysis solution was concentrated by conventional evaporating and spray-drying.

The product contained less than 2% by weight of glucose and cellobiose. When the same hydrolysis was carried out with the original cellulase enzyme preparation of Trichoderma reesei-fungus, the amount of produced glucose and cellobiose was above 5% by weight.

(ii) Hydrolysis with Aspergillus and Penicillium derived enzyme preparations

The enzyme preparations selected were commercially available Cellulase AP 3 (Amano Pharmaceutical Co., Ltd., Nagoya, Japan) produced using an Aspergillus strain and Cellulase CP (Sturge Enzymes, North Yorkshire, England) produced using a Penicillium strain. Carboxymethylcellulose hydrolysates were prepared as described in Example c(1), except that 30g of CMC-7MFD was used in 1 l of water, and the amounts of enzymes added were 0.028 g of Cellulase AP 3 (having a total endo-1, 4 beta-glucanase activity of 1350 nkat) and 0.048 g of Cellulase CP (having a total endo-1, 4

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beta-glucanase activity of 1350 nkat). The viscosities and molecular weight distributions of the hydrolysates produced by either cellulase were similar to the hydrolysate produced with enzymes derived from Trichoderma reesei.

The viscosities of the various cellulose derivatives and their hydrolysates as described above were measured using a Haake-Rotovisco viscometer with sensor systems NV (Karlsruhe, Federal Republic of Germany) (Table 2). The viscosities were measured in water solutions at 25°C. Table 2 sets forth the concentrations (by weight) of a variety of solutions all having the same viscosity.

TABLE 2

Concentrations of cellulose derivatives and their respective hydrolysates in solution all having a viscosity of 20 mPa.s (milli-Pascals-second) at 25°C.

Cellulose Derivative	Concentration (by weight)
Methylcellulose	2%
Methylcellulose hydrolysate	5%
Hydroxypropylmethylcellulose	3%
Hydroxypropylmethylcellulose hydrolysate	10%
Carboxymethylcellulose	2%
Carboxymethylcellulose hydrolysate	20%

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As the data in Table 2 indicates, the hydrolysate of a cellulose derivative has a substantially lower viscosity than an equal amount by weight in aqueous solution of the cellulose derivative itself. Thus, the hydrolysate can be incorporated into a foodstuff in substantially higher quantity as a fat or carbohydrate substitute than the cellulose derivative itself without compromising the texture, volume, density or the like of the foodstuff.

Example 8: Chemical Hydrolysis

2 gms of carboxymethylcellulose (Blanose Cellulose Gum 7 LFD, Hercules Chemical Co., 92507, Ruell-Malmaison Cedar, France) was hydrolyzed for about one hour in 100 ml of 1M sulphuric acid solution at about 100°C. After hydrolysis the solution was cooled to about room temperature, neutralized to about pH 6 with 25 ml of 25% (w/w) of NaOH solution and freeze-dried. This hydrolysis treatment produced a mixture of polymers containing less than about 4% by weight of saccharides (glucose). The viscosity (and average DP) of this hydrolysate is similar to the viscosities (and average DP) of the hydrolysates produced by the enzymatic treatments described above utilizing enzymes derived from Trichoderma reesei.

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All of the CMC hydrolysates described above can likewise be used to replace all or a portion of the normal high calorie content of a foodstuff, i.e. at least about 10% by weight.

Degradations of other polysaccharide derivatives as described above can be carried out with appropriate enzymes, chemical hydrolysis techniques or physical means to produce low calorie, edible polymeric mixtures having fat-like or carbohydrate-like eating qualities.

Although degraded starch and cellulose derivatives are most preferred, other degraded polysaccharide derivatives having branched or straight chain backbones comprising one or more of the monomer units glucose, galactose, arabinose, mannose, fructose, rhamnose, xylose and other sugar monomers are suitable.

It will now be apparent to those skilled in the art that other embodiments, improvements, details and uses can be made consistent with the letter and spirit of the foregoing disclosure and within the scope of this patent, which is limited only by the following claims, construed in accordance with the patent law, including the doctrine of equivalents.

What is claimed is:

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CLAIMS

1. A foodstuff composition comprising a mixture of polymers derived from degradation of a polysaccharide derivative, the derivative including one or more substituents, wherein the mixture of polymers has an average degree of polymerization in the range of 5-500.
2. The foodstuff composition of claim 1 wherein the substituents are selected from the group of carboxymethyl, hydroxyethylmethyl, methyl, hydroxypropyl, methylethyl, hydroxyethyl, hydroxypropylmethyl, sulfate, carboxylic acid, carboxylic acid ester and pyruvate.
3. The foodstuff composition of claim 1 wherein the mixture of polymers is substituted for at least a portion of a high calorie ingredient of the foodstuff composition.
4. The foodstuff composition of claim 3 wherein the high calorie ingredient is selected from the group of fats and carbohydrates.
5. The foodstuff composition of claim 3 wherein at least about 10 percent of the high calorie ingredient is removed from the food composition.

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6. The foodstuff composition of claim 3 wherein the mixture of polymers is substituted for the entire portion of the high calorie ingredient of the foodstuff composition.

7. The foodstuff composition of claim 1, wherein the substituents are substituted on the polysaccharide derivative to a degree of 0.1 to 3.

8. The foodstuff composition of claim 1, wherein the polysaccharide is selected from cellulose, starch, carrageenan, pullulan, pustulan, alginate, laminarin, guar gum, gum arabic, inulin, pectin, whelan, rhamsan, gellan, xanthan, zooglan, methylan, chitin, cyclodextrin and chitosan.

9. A foodstuff composition comprising a fat ingredient, water and one or more additional ingredients selected from the group of sweeteners, flours, emulsifiers, raising agents, thickeners, acidifiers and stabilizers wherein at least a portion of the fat ingredient is substituted by a mixture of polymers derived from a degraded polysaccharide derivative, the polymeric mixture having an average degree of polymerization in the range of 5 to 500.



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10. The foodstuff of claim 9 wherein the polysaccharide is selected from cellulose, starch, carrageenan, pullulan, pustulan, alginate, laminarin, guar gum, gum arabic, inulin, pectin, whelan, rhamsan, gellan, xanthan, zooglan, methylan, chitin, cyclodextrin and chitosan.

11. The composition of claim 10, wherein the polysaccharide derivative is substituted with one or more substituents selected from the group of carboxymethyl, methyl, hydroxyethylmethyl, hydroxypropyl, methylethyl, hydroxyethyl, hydroxypropylmethyl, sulfate, carboxylic acid, carboxylic acid ester and pyruvate.

12. The composition of claim 9 wherein at least about 10% of the fat ingredient is removed from the composition.

13. The composition of claim 11, wherein the mixture of polymers is substituted for the entire portion of the high calorie fat ingredient of the foodstuff composition.

14. The composition of claim 10, wherein the polysaccharide derivative is substituted to a degree of 0.1 to 3.

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15. The composition of claim 14, wherein the polysaccharide derivative is a starch derivative.

16. A cake composition comprising:

- (a) a fat ingredient;
- (b) a sweetener;
- (c) a flour;
- (d) a raising agent;
- (e) egg ingredient; and
- (f) water

wherein at least a portion of the fat ingredient is substituted by a mixture of polymers derived from a degraded polysaccharide derivative, the polymeric mixture having an average degree of polymerization in the range of 5 to 500.

17. The cake composition of claim 16, wherein the polysaccharide is selected from cellulose, starch, carrageenan, pullulan, pustulan, alginate, laminarin, guar gum, gum arabic, inulin, pectin, whelan, rhamsan, gellan, xanthan, zooglan, methylan, chitin, cyclodextrin and chitosan.

18. The cake composition of claim 17 wherein the polysaccharide derivative is substituted with one or more substituents selected from the group of carboxymethyl, methyl, hydroxyethylmethyl,

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hydroxypropyl, methylethyl, hydroxyethyl,  
hydroxypropylmethyl, sulfate, carboxylic acid,  
carboxylic acid ester and pyruvate.

19. The cake composition of claim 16 wherein at least about 10% of the fat ingredient is removed from the composition.

20. The cake composition of claim 19, wherein the mixture of polymers is substituted for the entire portion of the high calorie ingredient of the foodstuff composition.

21. The cake composition of claim 18 wherein the polysaccharide derivative is substituted to a degree of 0.1 to 3.

22. An icing composition comprising:

- (a) a fat ingredient;
- (b) a sweetener; and
- (c) water

wherein at least a portion of the fat ingredient is substituted by a mixture of polymers derived from a degraded polysaccharide derivative, the polymeric mixture having an average degree of polymerization in the range of 5 to 500.

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23. The icing composition of claim 22, wherein the polysaccharide is selected from cellulose, starch, carrageenan, pullulan, pustulan, alginate, laminarin, guar gum, gum arabic, inulin, pectin, whelan, rhamsan, gellan, xanthan, zooglan, methylan, chitin, cyclodextrin and chitosan.

24. The composition of claim 23 wherein the polysaccharide derivative is substituted with one or more substituents selected from the group of carboxymethyl, methyl, hydroxyethylmethyl, hydroxypropyl, methylethyl, hydroxyethyl, hydroxypropylmethyl, sulfate, carboxylic acid, carboxylic acid ester, pyruvic acid and pyruvate.

25. The composition of claim 22 wherein at least about 10% of the fat ingredient is removed from the composition.

26. The icing composition of claim 22 wherein the mixture of polymers is substituted for the entire portion of the high calorie ingredient of the foodstuff composition.

27. The composition of claim 24 wherein the polysaccharide derivative is substituted to a degree of 0.1 to 3.

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28. A method for preparing a low calorie food product comprising replacing at least a portion of a high calorie ingredient of a high calorie foodstuff composition with a mixture of polymers derived from degradation of a polysaccharide derivative, the mixture of polymers having an average degree of polymerization in the range of 5 to 500.

29. The method of claim 28 wherein the high calorie ingredient is selected from the group of fat and carbohydrate.

30. The method of claim 28, wherein the polysaccharide is selected from cellulose, starch, carrageenan, pullulan, pustulan, alginate, laminarin, guar gum, gum arabic, inulin, pectin, wheilan, rhamsan, gellan, xanthan, zooglan, methylan, chitin, cyclodextrin and chitosan.

31. The method of claim 30 wherein the polysaccharide derivative is substituted with one or more substituents selected from the group of carboxymethyl, methyl, hydroxyethylmethyl, hydroxypropyl, methylethyl, hydroxyethyl, hydroxypropylmethyl, sulfate, carboxylic acid, carboxylic acid ester and pyruvate.

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32. The method of claim 28 wherein at least about 10% of the high calorie ingredient is replaced.

33. The method of claim 28, wherein the mixture of polymers is substituted for the entire portion of the high calorie ingredient of the foodstuff composition.

34. The composition of claim 31 wherein the polysaccharide derivative is substituted to a degree of 0.1 to 3.

35. In a foodstuff composition, the improvement comprising the substitution of a mixture of polymers derived from degradation of a polysaccharide derivative for at least a portion of a high calorie ingredient of the foodstuff, wherein the mixture of polymers has an average degree of polymerization in the range of 5 to 500.

36. The composition of claim 35, wherein the polysaccharide is selected from cellulose, starch, carrageenan, pullulan, pustulan, alginate, laminarin, guar gum, gum arabic, inulin, pectin, whelan, rhamsan, gellan, xanthan, zooglan, methylan, chitin, cyclodextrin and chitosan.

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37. The improvement of claim 36 wherein the polysaccharide derivative is substituted with one or more substituents selected from the group of carboxymethyl, methyl, hydroxyethylmethyl, hydroxypropyl, methylethyl, hydroxyethyl, hydroxypropylmethyl, sulfate, carboxylic acid, carboxylic acid ester, pyruvic acid and pyruvate.

38. The improvement of claim 35 wherein at least about 10% of the high calorie ingredient is removed from the composition.

39. The improvement of claim 35, wherein the mixture of polymers is substituted for the entire portion of the high calorie ingredient of the foodstuff composition.

40. The improvement of claim 37 wherein the polysaccharide derivative is substituted to a degree of 0.1 to 3.

41. The improvement of claim 37, wherein the high calorie ingredient is selected from the group of fat and carbohydrate.

42. The composition of claim 8, wherein the mixture of polymers has an average degree of polymerization in the range of 7-200.

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43. The composition of claim 11, wherein the mixture of polymers has an average degree of polymerization in the range of 7-200.

44. The composition of claim 17, wherein the mixture of polymers has an average degree of polymerization in the range of 7-200.

45. The composition of claim 23, wherein the mixture of polymers has an average degree of polymerization in the range of 7-200.

46. The composition of claim 30, wherein the mixture of polymers has an average degree of polymerization in the range of 7-200.

47. The composition of claim 36, wherein the mixture of polymers has an average degree of polymerization in the range of 7-200.